

REMARKS

Reconsideration and allowance of this application are respectfully requested in light of the foregoing amendments and the following remarks.

Allowed Claims

Applicant acknowledges and appreciates the Examiner's allowance of claims 12-20 of the instant application.

Claim Status

Claims 1 and 11 were amended. Claim 2 was canceled. Claims 1-11 are pending. Claims 12-20 are allowed. No new matter was added.

Double Patenting Rejection

Claims 1-9 and 11 stand provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-10 of co-pending Application No. 10/588,695. Applicant traverses.

Applicant is filing a terminal disclaimer herewith, with reference to co-pending Application No. 10/588,695 filed on February 15, 2005. In light of this action, Applicant requests

that the Examiner remove the provisional rejection of claims 1-9 and 11 and the claims be allowed.

§112 Claim Rejections

Claim 11 stands rejected under 35 U.S.C. §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Applicant traverses.

Applicant has amended claim 11 to further limit claim 1 from which it depends. In light of this amendment, Applicant requests that the Examiner remove the rejection of claim 11 and the claim be allowed.

§102 Claim Rejections

Claims 1, 9, and 11 stand rejected under 35 U.S.C. §102(b) as being anticipated by U.S. Patent No. 5,290,448 (hereinafter Sluma). Applicant traverses.

As stated in the previous office action, to anticipate a claim under 35 U.S.C. §102(b), a single source must contain all of the elements of the claim. *See Hybritech Inc. v. Monoclonal Antibodies, Inc.*, 802 F.2d 1367, 1379, 231 USPQ 81, 90 (Fed. Cir. 1986); *Atlas Powder Co. v. E.I. du Pont De Nemours & Co.*,

750 F.2d 1569, 1574, 224 USPQ 409, 411 (Fed. Cir. 1984); *In re Marshall*, 578 F.2d 301, 304, 198 USPQ 344, 346 (C.C.P.A. 1978). Missing elements may not be supplied by the knowledge of one skilled in the art or the disclosure of another reference. See *Structural Rubber Prods. Co. v. Park Rubber Co.*, 749 F.2d 707, 716, 223 USPQ 1264, 1271 (Fed. Cir. 1984). Where a reference discloses less than all of the claimed elements, an Examiner may only rely on PCT Article 33(3). See *Titanium Metals Corp. v. Banner*, 778 F.2d 775, 780, 227 USPQ 773, 777 (Fed. Cir. 1985).

There appears to be a misunderstanding by the Examiner with respect to the feature of the membranes according to the instant invention regarding the following language from amended claim 1:

in the absence of additives stabilizing the pores in the membrane wall and after prior drying, has a maximum sieving coefficient for albumin of 0.005 combined with a sieving coefficient for cytochrome c that satisfies the relation

$$SC_{cc} \geq 5 \cdot 10^{-5} \cdot UFR_{Alb}^3 - 0.004 \cdot UFR_{Alb}^2 + 0.1081 \cdot UFR_{Alb} - 0.12$$

Thus, as described in the previous office action, the membranes of the instant invention possess the above sieving coefficients without a stabilization of the pores. More specifically, the membranes of the instant invention possess the above sieving coefficients without the necessity of additives such as glycerol

or polyethylene glycol. (See also pages 13-19 of the Response to the previous office action).

By this feature, the membranes of the instant invention differ from membranes disclosed in Sluma which require a stabilization of the pores in order to obtain sieving coefficients as specified in claim 1. In order for membranes disclosed in Sluma, to achieve the same sieving coefficients, it is necessary to stabilize the pores. Otherwise the membranes disclosed in Sluma would not exhibit the required sieving coefficient for cytochrome c in combination with a very low sieving coefficient for albumin. **These prior art membranes must be treated or impregnated with stabilizers (e.g., with a glycerol/water solution) prior to drying in order to stabilize the pores.** The pores are filled with the glycerol/water solution and during drying, the water evaporates away, leaving the glycerol behind which acts to stabilize the pores. Without this stabilization, the membranes disclosed in Sluma, most specifically the small pores in the separation layer of such membranes, would shrink during drying, thus altering the separation characteristic and shifting the exclusion limit to smaller molecule sizes. This would mean that middle molecules (i.e., cytochrome c would be retained by the Sluma membrane,

resulting in comparably low sieving coefficients for cytochrome C.

The membrane disclosed in Sluma would fail to achieve the sieving coefficient requirements of claim 1 without the addition of stabilizers or if the stabilizers were washed out of the membrane's pores prior to drying the membrane. The membrane in Sluma would fail because without the stabilizers, the pores would shrink as described above, resulting in a change to the separation characteristic and a reduction of the sieving coefficient. This should come as no surprise as it is well known in the prior art that membranes, and specifically ultrafiltration membranes often require the use of pore stabilizers, also called plasticizers or softeners, prior to drying in order to maintain the desired characteristics of the membrane. Looking to pages 142-43 (attached hereto) of the Handbook of Industrial Membrane Technology (1988), written by Mark C. Porter where it states that "Plasticizers are necessary...if they are to be dried, to prevent collapse of the pores during drying." See also pages 149-51 (attached hereto) of Synthetic Polymeric Membranes - A Structural Perspective (1985), written by Robert E. Kesting.

Looking to the art cited by the Examiner, Heilmann (U.S. Patent No. 4,906,375) wherein it states that the fiber,

undergoes a drying process to remove residual water therein, stemming from the process of manufacture, more or less completely. The outcome of this is that-- as we have seen--the small pores become filled with air and for this reason are not able to play any part when the filter is used with water. It is only the large pores that are available for the water that is to be ultrafiltered, with the consequence that the rate of ultrafiltration as a whole is cut down and the solute separation properties of the membrane are altered. The above remarks also apply insofar as it is a question of the mechanical properties of such a membrane and the processing thereof.

(Column 1, Line 57 - Column 2, Line 2). See also EP 0 716 859 A2 which is cited in the instant application, that impregnation of a membrane with glycerine is utilized in order to maintain the membrane structure and that the performance of a membrane may be influenced by the concentration of glycerin used for impregnation. (Page 8, Lines 15-17 and 26-28).

The membranes disclosed in Sluma are all treated with a softener or pore stabilizer prior to drying. (See Sluma, Column 3, Lines 36-39, Column 4, Lines 11-14, and Example 1). Additionally, the membranes described in Example 3 are post-treated with a glycerin/water mixture. The conditions and parameters used in Example 3 refer back to Example 2, and Example 2 uses the same process described in Example 1. Example 1 specifically states that, "[T]he hollow fiber thus produced

was rinsed intensely to remove the solvent residue, after treated for 1 minute with a mixture of 20 wt.% glycerine in water at 20°C., and then dried at room temperature." (Column 7, Lines 13-16) Based on the language used in Example 1 in conjunction with the material disclosed in the Handbook of Industrial Membrane Technology above, it follows that Sluma makes intentional use of the softener bath to stabilize the structure of its membranes. This leads us to the obvious conclusion that without stabilization provided by the treatment described above, the structure of the membranes described in Sluma would be influenced or altered during drying, resulting in membranes possessing properties different than those described within Sluma. More Specifically, the membranes described in Sluma would exhibit a reduced permeability for middle molecules such as cytochrome c which would result in reduced sieving coefficients for cytochrome c if they were dried without prior treatment in a glycerin/water softener bath due to the dramatic effect on the small pores which are responsible for the separation characteristic.

Based on the foregoing evidence, it is obvious that the membranes disclosed in Sluma fail to fulfill the criterion of claim 1 of the instant application which requires that the sieving coefficients be determined for membranes which have been

dried in the absence of additives which stabilize the pores in the membrane wall. Additionally, based on the teachings of the above cited Handbook, Heilmann and EP 0 716 859 A2, it is obvious that the membranes disclosed in Sluma, if dried in the absence of the above described additives which act to stabilize the pores in the membrane wall, would fail to fulfill the relation given in claim 1 of the instant invention for the sieving coefficient for cytochrome c, SC_{cc} .

Accordingly, Sluma does not disclose all of the elements of claim 1. Therefore, claim 1 of the instant application is not anticipated by Sluma and this rejection must fail.

Additionally, the Examiner fully ignores the fact that Sluma fails to disclose a membrane having an integrally asymmetrical structure across its wall as required by claim 1 of the instant application. As described in our response to the previous office action, an integrally asymmetric membrane is a membrane with a separating layer and a supporting layer being formed together from the same material simultaneously during production of the membrane. The structure of these membranes according to the instant invention is such that when starting from the separating layer, the pore size in the support structure changes across the wall thickness in the membrane.

(Specification, Page 11 Line 26 - Page 12, Line 15). This is directly contradicted by Sluma where it is disclosed that there is no pore radius gradient above the skin. (Column 2, Lines 51-53).

Additionally, the Examiner argues on Page 4 of the current office action that Example 3 from Sluma satisfies the relation for the sieving coefficient. Newly amended claim 1 refutes this argument. In addition to the fact that the sieving coefficients of Sluma are not determined on non-stabilized membranes as required by claim 1 of the instant invention, amended claim 1 now requires that the ultrafiltration rate in albumin given in Example 3 of Sluma [$UF_{R_{alb}} = 13 \text{ ml/h(m}^2\text{)(mmHg)}$] a sieving coefficient for cytochrome c, SK_{cc} , of 0.72. The value given for the sieving coefficient cytochrome c in Example 3 of Sluma is 0.61, which is well below the value required by newly amended claim 1.

In reference to claims 9 and 11, "[I]f an independent claim is not anticipated by prior art, then its dependent claims, which necessarily include the limitations of the independent claim, are not anticipated either. *Kovin Assoc. v. Extech/Exterior Technologies*, 2006 U.S. Dist. LEXIS 63250 (N.D. Ill. 2006), citing *Trintec Indus., Inc. v. Top-U.S.A. Corp.*, 295

F.3d 1292, 1296 (Fed. Cir. 2002). Thus, claims 9 and 11 are not unpatentable over Sluma and should be allowed.

Claims 1-9 and 11 stand rejected under 35 U.S.C §102(b) as anticipated by or, in the alternative, under 35 U.S.C. §103(a) as obvious over U.S. Patent No. 6,565,782 (hereinafter Wang). Applicant traverses.

Wang does not disclose a hydrophilic, water-wettable, semi-permeable hollow fiber membrane for blood purification as is described in claim 1 of the instant invention. The Examiner argues that the membranes disclosed in Wang inherently possess an ultrafiltration rate and sieving coefficients for albumin and cytochrome c simply because some structural features required by claim 1 of the instant invention are met. This argument is baseless and simply incorrect. The Examiner overlooks the fact that the ultrafiltration rate and sieving coefficient, both key features of the instant invention, are strongly related to the structural conditions of a membrane which are impossible to describe by simple geometric measures.

One skilled in the art would instantly recognize from the Title that Wang is related to microfiltration membranes. This is in stark contrast to the membranes disclosed in the instant

application which relate to membranes for hemodialysis or conventional hemofiltration. (Specification, Page 1, Paragraph 1). One skilled in the art would know that for microfiltration, membranes having pore sizes of the separation pores (minimum pore sizes, pore sizes of the pores in the separation layer) in the range of 0.5 to 2 μm are required. Again, this is in stark contrast to the ultrafiltration membranes of claim 1 of the instant application which are intended for hemodialysis or conventional hemofiltration and possess pore sizes that are significantly smaller than those required for microfiltration.

The differences between the membranes described in the instant application and the membranes described in Wang become even more evident when one considers the membrane features disclosed by each of the two groups. Looking to claim 1 of the instant invention, the membrane must have a maximum sieving coefficient for albumin of 0.005. This means that an extremely limited amount of albumin passes through the membrane wall. Instead, the albumin molecules are retained by the membrane which means the albumin remains in the blood. Human albumin has a molecular weight of about 65,000 Dalton which requires a membrane having a pore size of between 0.02 to 0.03 μm in order to retain the albumin. **A membrane having pores larger than 0.02**

to 0.03 μm would lack the ability to retain human albumin as is required by claim 1 of the instant invention.

Wang discloses membranes having a minimum pore size greater than 0.1 μm . (Column 5, Lines 25-28). One skilled in the art would clearly recognize that the membranes disclosed by Wang would lack the ability to retain human albumin resulting in a sieving coefficient for albumin of 1.0. This is several orders of magnitude away from the sieving coefficient for albumin of 0.005 required by claim 1 of the instant invention.

Looking again to Wang, we can see that the membranes described therein are highly asymmetric and have "minimum pore sizes greater than about 0.1 μm in a minimum pore surface and gradually increasing pore sizes throughout the substructure of the membrane to a coarse pored surface having pore sizes up to about 100 μm ." (Column 5, Lines 25-30). This means that the membranes of Wang have a rather coarse pored structure which results in high permeability/ultrafiltration rates for substances such as water. The membranes described by Wang exhibit such high permeability for water that they are actually at the upper range generally obtained by microfiltration membranes. Looking to the membranes in Example 1 of Wang, we see a microfiltration rate for water of 2000 ml/min/9.5 cm^2 at 10

psid. Example 2 illustrates a membrane having a microfiltration rate for water of 8000 ml/min/9.5 cm² at 10 psid. Recalculation of the value given in Example 1 of Wang into the dimension used in the instant application results in a water permeability of 240,000 ml/h(m²) (mmHg). Taking into consideration as a first approximation a factor of 10 for the relation between the filtration rate for water and the filtration rate in albumin solution, an ultrafiltration rate in albumin solution of 24,000 ml/h(m²) (mmHg) would result for the membranes disclosed in Example 1 of Wang. This exceeds the ultrafiltration rate in albumin solution according to claim 1 of the instant application (at most 23.5 ml/h(m²) (mmHg)) by roughly a factor of 10³.

Clearly, as demonstrated above, the membranes of the instant application differ significantly with respect to their structure (pore size in the separating layer) when compared to the membranes disclosed in Wang. Additionally, Wang discloses microfiltration membranes which, because of their open pored structure, possess membrane properties typically associated with microfiltration membranes unlike the ultrafiltration membranes disclosed by the instant application which may be used for hemodialysis or conventional hemofiltration with low exchange volumes respectively.

Accordingly, Wang does not disclose all of the elements of claim 1. Thus, clearly claim 1 is neither anticipated nor obvious over Wang and should be allowed. In reference to claims 3-9 and 11, "[I]f an independent claim is not anticipated by prior art, then its dependent claims, which necessarily include the limitations of the independent claim, are not anticipated either. *Kovin Assoc. v. Extech/Exterior Technologies*, 2006 U.S. Dist. LEXIS 63250 (N.D. Ill. 2006), citing *Trintec Indus., Inc. v. Top-U.S.A. Corp.*, 295 F.3d 1292, 1296 (Fed. Cir. 2002). Thus, claims 3-9 and 11 are neither anticipated nor obvious over Wang and should be allowed.

§103 Claim Rejections

Claims 3-8 stand rejected under 35 U.S.C. §103(a) as being obvious over U.S. Patent No. 5,290,448 (hereinafter Sluma) in view of U.S. Patent No. 4,906,375 (hereinafter Heilmannn). Applicant traverses.

The above comments regarding both Sluma and Heilmannn are incorporated herein. MPEP § 2143 "Basic Requirements of a *Prima Facie* Case of Obviousness" states:

To establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the

reference or to combine references teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all claim limitations.

Regarding the third criterion, the court has stated that "to establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art." *In re Royka*, 490 F.2d 981, 180 USPQ 580 (CCPA 1974).

As stated above, Sluma does not disclose a hydrophilic, water-wettable, semi-permeable hollow fiber membrane for blood purification in the absence of additives stabilizing the pores in the membrane wall and after prior drying as disclosed in claim 1. Again, without stabilization provided by the treatment described above, the structure of the membranes described in Sluma would be influenced or altered during drying, resulting in membranes possessing properties different than those described within Sluma. More Specifically, the membranes described in Sluma would exhibit a reduced permeability for middle molecules such as cytochrome c which would result in reduced sieving coefficients for cytochrome c if they were dried without prior treatment in a glycerin/water softener bath due to the dramatic effect on the small pores which are responsible for the separation characteristic.

Based on the foregoing evidence, it is obvious that the membranes disclosed in Sluma fail to fulfill the criterion of claim 1 of the instant application which requires that the sieving coefficients be determined for membranes which have been dried in the absence of additives which stabilize the pores in the membrane wall. Additionally, based on the teachings of the above cited Handbook, Heilmann and EP 0 716 859 A2, it is obvious that the membranes disclosed in Sluma, if dried in the absence of the above described additives which act to stabilize the pores in the membrane wall, would fail to fulfill the relation given in claim 1 of the instant invention for the sieving coefficient for cytochrome c, SC_{cc}.

Applicant contends that none of the prior art references, neither Sluma, nor Heilmann, alone or in combination, teach, suggest, or provide a motivation for making a hydrophilic, water-wettable, semi-permeable hollow fiber membrane for blood purification in the absence of additives stabilizing the pores in the membrane wall and after prior drying with all of the claim elements of claim 3, which is dependent on claim 1.

The prior art reference or combination of references relied upon by the Examiner must teach or suggest all of the limitations of the claims. See *In re Zurko*, 111 F.3d 887, 888-

89, 42 U.S.P.Q.2d 1467, 1478 (Fed. Cir. 1997); *In re Wilson*, 424 F.2d 1382, 1385, 165 U.S.P.Q. 494, 496 (C.C.P.A. 1970) ("All words in a claim must be considered in judging the patentability of that claim against the prior art."). The teachings or suggestions, as well as the expectation of success, must come from the prior art, not applicant's disclosure. See *In re Vaeck*, 947 F.2d 488, 493, 20 U.S.P.Q.2d 1438, 1442 (Fed. Cir. 1991). In this instance, from the information detailed above, it is clear that Sluma and Heilmannn fail to teach or suggest all the limitations of Applicant's claims.

Only hindsight reconstruction based upon the instant specification would lead the Examiner to the conclusion that the claims in the instant application are rejected under §103 as unpatentable over Sluma in view of Heilmannn. Accordingly, the instant rejection must be removed.

In reference to claims 4-8, dependent claims are nonobvious under section 103 if the independent claims from which they depend are nonobvious. *Hartness Int'l, Inc. v. Simplimatic Eng'g Co.*, 819 F.2d 1100, 1108, 2 USPQ2d 1826, 1831 (Fed. Cir. 1987); *In re Abele*, 684 F.2d 902, 910, 214 USPQ 682, 689 (CCPA 1982); see also *In re Sernaker*, 702 F.2d 989, 991, 217 USPQ 1, 3

(Fed. Cir. 1983). Thus, claims 4-8 are not unpatentable over Sluma in view of Heilmann and should be allowed.

Conclusion

In view of the foregoing, Applicant respectfully requests a Notice of Allowance in this application.

Respectfully submitted,



Blake E. Vande Garde
Attorney for Applicant
Reg. No. 58,264

Customer No. 29494
Hammer & Associates, P.C.
3125 Springbank Lane
Suite G
Charlotte, NC 28226
Telephone: 704-927-0400
Facsimile: 704-927-0485
H:\2037\008\Amendment042709.doc

HANDBOOK OF INDUSTRIAL MEMBRANE TECHNOLOGY

Edited by

Mark C. Porter

Consultant
Pleasanton, California

Copyright © 1990 by Noyes Publications

No part of this book may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission in writing from the Publisher.

Library of Congress Catalog Card Number: 88-17876

ISBN 0-8155-1205-8

Printed in the United States

Published in the United States of America by

Noyes Publications

Mill Road, Park Ridge, New Jersey 07656

10 9 8 7 6 5 4 3 2 1

Library of Congress Cataloging-in-Publication Data

Handbook of industrial membrane technology

Bibliography: p.

Includes index.

1. Membranes (Technology) -- Handbooks, manuals, etc.

I. Porter, Mark C.

TP159.M4H36 1988 660.2'842 88-17876

ISBN 0-8155-1205-8

The doctor blade on the solution trough is adjusted so as to meter a coating thickness on the drum or fabric between 100 and 500 μ in thickness. If the viscosity of the casting solution is such that it rapidly penetrates into the fabric, a greater thickness is required. Considerable attention must be given to obtaining the proper match between a reinforcing fabric and the viscosity of the casting solution. If there is too little penetration into the fabric, the bond between the membrane and the backing will be weak, resulting in membrane delamination. On the other hand, too much penetration will result in a considerable resistance to flow in the backing material, which is often thicker than the membrane itself.

It will be noted that the cast film is immersed in the nonsolvent (water) of the gel tank immediately and no roller touches the surface of the film until it is completely gelled. Indeed, the speed of the casting process is determined by the gelation time of the membrane and the physical dimensions of the gel tank. Because the gelation time for casting UF membranes with a liquid precipitant is much less than that for MF membranes with a gaseous precipitant, UF casting machines have a much higher rate of output. A 60 foot long casting machine with environmental chambers for casting MF membranes may run as slowly as one foot per minute. A 10 foot long casting machine with gel tank for casting UF membranes may run as fast as ten feet per minute—an order of magnitude faster than the MF caster. Therefore, contrary to popular myth, UF membranes are often less expensive to make than MF membranes. This cost difference is accentuated by the fact that an MF caster must often run for an hour before any product comes off the machine. The feedback for adjustments to the process is greatly delayed resulting in considerable waste material before conditions in the environmental chambers are set. With a UF caster, product is produced almost immediately and feedback is rapid. Further, the process is much simpler than that required to make MF membranes.

It is advisable to use DI water in the gel tank. The author has successfully cast many large batches of UF membranes using tap water in the quench bath. However, this often results in membrane product which is discolored (iron oxide) and variable with the seasons as the tap water quality changes. DI water with an 18M Ω resistivity is the best standard. However, it must be borne in mind that high resistivity water will result in faster leach rates of solvent from the gelling casting solution which may affect the pore size of the final membrane.

When producing membranes for use in the pharmaceutical industry, the use of depyrogenated water is required. Otherwise, pyrogens will be incorporated in the cast membrane and some will leach out in the filtrate with use. Depyrogenization may be accomplished by filtering water from the ion exchange columns with a 10,000 MWCO UF membrane.

Water in the gel bath must be replaced periodically or better yet, continuously to minimize the buildup of solvents or other contaminants in the quench bath. If bacteria slime or turbid water is noted, the tank should be drained and cleaned.

Though Figure 3.4 shows the rinse tank adjacent to the gel tank with continuous rinsing of the cast/precipitated product, in practice it is a separate operation. This is necessary because of the long residence times required in the rinse tank to remove final traces of solvents from the membrane. A separate tank may also be used to apply wetting agents or plasticizers.

Plasticizers are necessary for some membranes, if they are to be dried, to

meter a coating
ness. If the vis-
to the fabric, a
n to obtaining
of the casting
d between the
delamination.
able resistance
membrane itself.
ent (water) of
film until it is
rmined by the
ie gel tank. Be-
I precipitant is
nt, UF casting
asting machine
in as slowly as
ank for casting
of magnitude
JF membranes
st difference is
our before any
to the process is
nditions in the
duced almost
h simpler than

as successfully
e quench bath.
ored (iron ox-
. DI water with
e in mind that
om the gelling
ane.
dustry, the use
ncorporated in
Depyrogeniza-
range columns

r yet, continu-
in the quench
be drained and

tank with con-
separate opera-
ed in the rinse
are tank may

prevent collapse of the pores during drying. Figure 3.5 shows the capillary stress in the small pores of a UF membrane during drying.

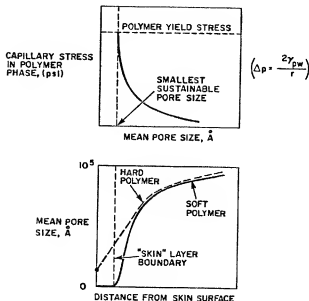
$$(1) \quad \Delta P = \frac{2\gamma}{r}$$

where ΔP = the pressure difference across the curved interface between the liquid and gas.

γ = the surface tension of the liquid in the pores ($\gamma = 72$ dynes/cm for water).

r = radius of curvature of the interface (equal to the radius of the pore for perfectly wetting or perfectly nonwetting pores).

The pores of UF and RO membranes are small enough that the capillary stresses at the air-water interface can exceed the yield strength of "soft" polymers. Hydrophobic polymers like PVDF can be dried without irreversible damage to the pores, but must be rewetted to initiate flow. "Hard" polymers with the larger pore sizes can also be dried without ill-effect. The "soft" polymers can be dried if the surface tension of the liquid filling the pores is reduced. This may be accomplished by replacing the water with a low boiling organic like alcohol or acetone which has a low surface tension and can be evaporated without creating large capillary stresses. Alternatively, a 15% solution of glycerin or polyethylene glycol in water or isopropanol can be used to saturate the pores prior to drying. This not only reduces the surface tension, but the glycol remains behind after drying-serving as a plasticizer and wetting agent in the dry membrane. This latter method is used by most manufacturers who ship "dry" membranes.



SYNTHETIC POLYMERIC MEMBRANES

A Structural Perspective
Second Edition

ROBERT E. KESTING
IRVINE, CALIFORNIA

*This book
the occasion
invention of
membrane
attention to
homogeneous
ment that
membranes.*

Copyright © 1985 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data:

Kesting, Robert E., 1933-

Synthetic polymeric membranes.

"A Wiley-Interscience publication."

Includes bibliographies and index.

1. Membranes (Technology) 2. Polymers and polymerization. I. Title.

TP159.M4K4 1985 660'.28424 85-6162
ISBN 0-471-80717-6

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

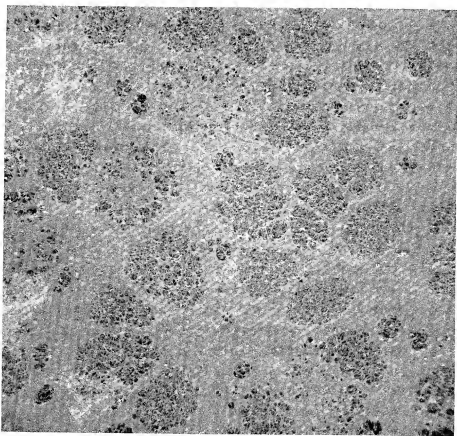


FIGURE 711. SEM photomicrograph of the top surface of a dry cellulose acetate membrane with a nonintegral skin.

(Table 7.4). In hydrophobic sols water acts both to hasten gelation and to increase the size of voids in the gel structure. This is attributable to two factors: (1) a high degree of incompatibility with the solvated polymer component of the casting solution; and (2) high surface tension. Both factors act to cause water to separate from the remainder of the solution and nucleate comparatively large micelles which then result in coarse microgels. The presence of a microgel structure in membranes from polymers such as the cellulose and the polyamides which possess some affinity for water confers the important property of wet-dry reversibility on these membranes.⁶ This is so because the magnitude of the capillary forces which come into play upon drying depends on the internal surface area of the membrane which in turn depends on the cell size. Microgel membranes possess large (1–10 μm di-

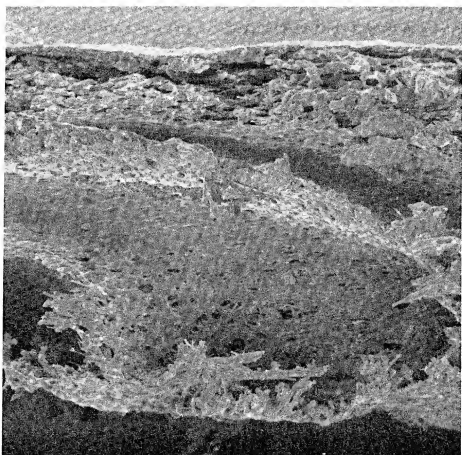


FIGURE 7.12. SEM photomicrograph of a cross section of a dry cellulose acetate membrane with a nonintegral substructure (from Kesting et al.¹⁴, © 1965).

TABLE 7.2 EQUIVALENT NONSOLVENT CONCENTRATIONS IN ACETONE AND DIOXOLANE SOLUTIONS^a FOR DRY-RO BLEND MEMBRANES OF CA AND THE TMA SALT OF CA 11-BROMOUNDECANOATE

Solvent	Boiling Point (°C)	Δbp (°C)	Nonsolvent Concentration (g IBA/formulation)	Permeability ^a (gal/ft ² day)	Salt ^b Rejection (%)
Acetone	56	54	38	5.6	97.9
Dioxolane	75	35	54	5.5	97.8

^aTotal polymer concentration, 10% wt/vol; polymer ratio, 6/1 JLF-68CA/TMA salt of CA 11-bromoundecanoate (made from E-383-40 CA with 0.3-DS (quaternary ammonium groups); methanol, 10 g/formulation.

^b0.5% NaCl feed at 400 psi and $25 \pm 1^\circ\text{C}$.

TABLE 7.3 EFFECT OF RELATIVE HUMIDITY ON PORE SIZE^a

Relative Humidity at 20°C (%)
80
60
40

^aFrom Maier and Sch

^bFor 500 mL H₂O/12.

TABLE 7.4 INFLUENCE OF PORE SIZE AND PERMEABILITY ON CASTING SOLUTION

H₂O Concentration in Casting Solution (%)

3.3
0.4
0.0 (trace)

^aFrom Maier and Schuermans

^bFor 500 mL H₂O/12.5 cm² a

porosity during drying process tends to employ (both of which characterize wet process, the former ever, there are many examples by a wet process

7.3 THE WET PROCESS

The wet or combined evaporation inversion process in which the solvent system for non-swollen membranes; morphology in the dry process characteristics. It is there

TABLE 7.3 EFFECT OF RELATIVE HUMIDITY UPON PERMEABILITY AND PORE SIZE^a

Relative Humidity at 20°C (%)	Filtration Time ^b (sec)	Average Pore Diameter (nm)
80	25-40	~ 600
60	40-60	~ 500
40	60-80	~ 400

^aFrom Maier and Scheuermann⁴^bFor 500 mL H₂O/12.5 cm² at 70 cm HgTABLE 7.4 INFLUENCE OF CASTING SOLUTION WATER CONCENTRATIONS UPON PORE SIZE AND PERMEABILITY OF COLLODION MEMBRANES^a

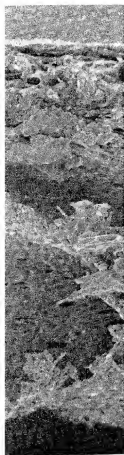
H ₂ O Concentration in Casting Solution (%)	Filtration Time ^b (S)	Average Pore Diameter (nm)	Casting-Solution Viscosity at 20°C (cps)
3.3	40	600	2011
0.4	800	30	1813
0.0 (trace)	4000	15	1600

^aFrom Maier and Scheuermann⁴^bFor 500 mL H₂O/12.5 cm² at 70 cm Hg.

porosity during drying and less likely to be wet → dry reversible. Since the dry process tends to employ more dilute solutions and less compatible pore formers (both of which characteristics promote the formation of microgels) than does the wet process, the former is more likely to produce microgels than the latter. However, there are many exceptions to this rule and it is possible both to produce microgels by a wet process and ultragels by a dry process.

7.3 THE WET PROCESS

The wet or combined evaporation-diffusion technique is that variation of the phase-inversion process in which a viscous polymer solution is either (1) allowed to partially evaporate after which it is immersed into a nonsolvent gelation bath where whatever is left of the solvent-pore-former system is exchanged for the nonsolvent



se acetate membrane with a

N ACETONE AND
F CA AND THE TMA

Permeability ^a gal/ft ² day)	Salt ^b Rejection (%)
5.6	97.9